

Updated: 13 November 2013

CEE697K Lecture #14 1

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# CEE 697K

## ENVIRONMENTAL REACTION KINETICS

### Lecture #14

**Prediction Methods:** Going beyond

Hammett II

Brezonik, pp.553-578

David A. Reckhow

Introduction

## Oxidation I

2

### □ 3D QSAR models

**Table 12.10**  
**Descriptors and properties generated by QikProp used for QSPR model development**

Descriptor/Property	Explanation
<b>Molecular descriptor</b>	
MW, volume	Molecular weight and volume
SASA, FOSA, FISA, PISA, WPSA	Molecular surface area, hydrophobic, hydrophilic, $\pi$ and weakly polar component of surface area
#amine, #amidine, #acid, #amide	Number of non-conjugated functional groups for each type
#rotor	Number of non-trivial (not CX <sub>3</sub> ), non-hindered (not alkene, amide, small ring) rotatable bonds
#rctvFG, #metabol	Number of reactive functional groups, number of metabolites
donorHB, acptHB	Number of hydrogen bonding donated or accepted by the solute from water
dipole	Dipole moment
QPpolrz	Polarizability
IP, EA	Ionization potential and electron affinity
<b>Physicochemical properties</b>	
S	Solubility
QplogPC16	Hexadecane/gas partition coefficient
QPlogPoc	Octanol/gas partition coefficient
QPlogPw	Water/gas partition coefficient
QplogPo/w	Octanol/water partition coefficient

Snyder et al., 2007 "Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes" [AWWARF final report]

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# Oxidation II

3

## results

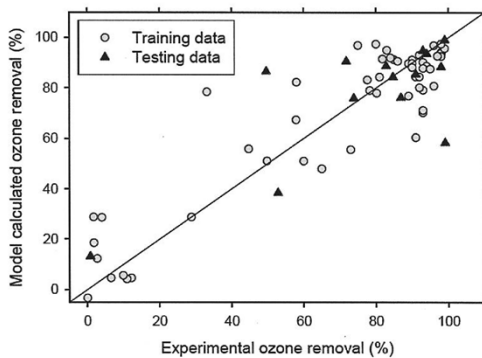


Figure 12.4 Comparison between the experimental obtained ozone removal of selected EDCs and PPCPs and model calculated results

Snyder et al., 2007 "Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes" [AWWARF final report]

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# UF I

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## Stepwise addition

Table 12.11  
Evolution of significant dependent variables in QSPR modeling for the UF membrane

# of descriptors	#acid	H bond	QPpolarz	#amide	IP	QPlogS	Log Kow	R <sup>2</sup>
6	√	√	√	√	√	√	x	0.645
5	√	√	√	√	√	x	x	0.643
4	√	√	√	√	x	x	x	0.638
3	√	√	√	x	x	x	x	0.615
2	√	x	x	x	x	x	√	0.562
1	x	x	x	x	x	x	√	0.396

T value decreasing →

Note: √ indicates a parameter found significant in the model and x indicates a parameter excluded from the model

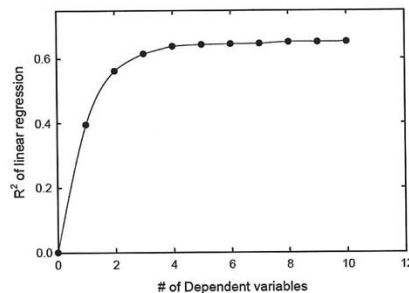


Figure 12.5 Progress in R<sup>2</sup> as the number of dependent variables increases

Snyder et al., 2007 "Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes" [AWWARF final report]

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## UF II

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## □ results

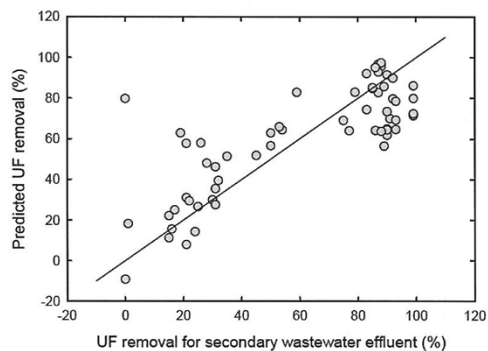


Figure 12.6 Comparison between the experimental obtained UF removal of selected EDCs and PPCPs and model calculated results

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## Acid/Base

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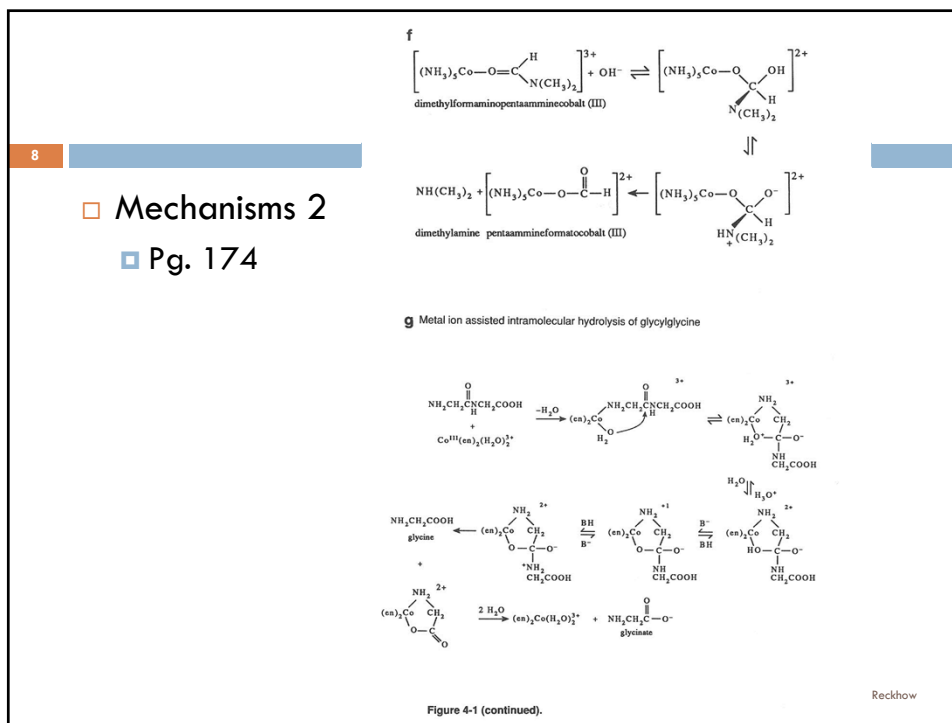
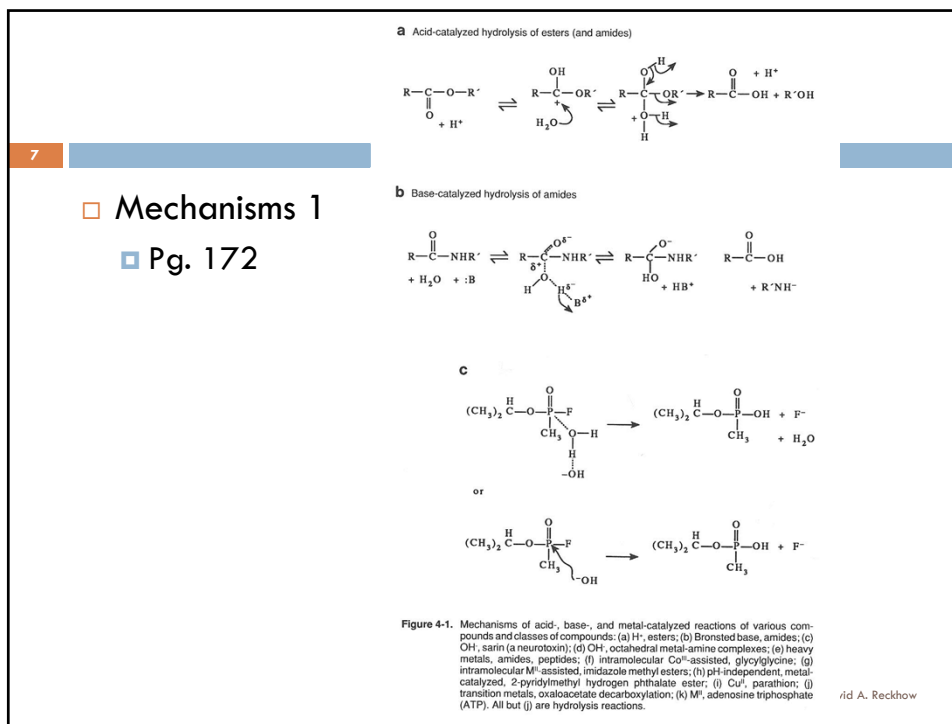
□ Summary reactions  
 □ Pg.171 in Brezonik

Table 4-1. Mechanisms of Acid-Base Catalysis

Type	Mechanism	Rate expression	Comments
I. Specific H <sup>+</sup>	$S + HA \xrightleftharpoons[k_2]{k_1} SH^+ + A^-$ $SH^+ + H_2O \xrightarrow[\text{slow}]{k_3} P + H_3O^+$	$P = \frac{k_1 k_3 [S][HA][A^-]}{(k_2 + k_1 k_3 / K_a)[S][H^+]}$ where $K_a = \frac{[H^+][A^-]}{[HA]}$	For protolytic case, expression applies when $k_3 \ll k_2[A^-]$ ; whether initial H <sup>+</sup> transfer is from Bronsted acid (HA) or H <sub>3</sub> O <sup>+</sup> .
II. General acid	$S + HA \xrightleftharpoons[k_2]{k_1} SH^+ + A^-$ $SH^+ + H_2O \xrightarrow[\text{fast}]{k_3} P + H_3O^+$	$P = [S](\sum k_i[HA])$	Expression applies when $k_3 \gg k_2[A^-]$ ; rate-controlling step is formation of intermediate SH <sup>+</sup> ; P written for presence of several Bronsted acids in system.
III. General acid	$S + HA \xrightleftharpoons[k_2]{k_1} SH^+ + A^-$ $SH^+ + A^- \rightarrow P + HA$	$P = \frac{k_1 k_3 [S][HA]}{(k_2 + k_3)}$ or $P = k[S][HA]$	Protolytic mechanism yields general acid catalysis regardless of relative sizes of $k_2$ and $k_3$ .
IV. Specific OH <sup>-</sup>	$HS + B \xrightleftharpoons[k_2]{k_1} S^- + BH^+$ $S^- + H_2O \xrightarrow[\text{slow}]{k_3} P + OH^-$	$P = \frac{k_1 k_3 [S^-][B][OH^-]}{(k_2 + k_1 k_3 / K_b)[S][OH^-]}$	For protolytic case, expression applies when $k_3 \ll k_2[BH^+]$ regardless of nature of proton acceptor in first step.
V. General base	$HS + B \xrightleftharpoons[k_2]{k_1} S^- + BH^+$ $S^- + H_2O \xrightarrow[\text{fast}]{k_3} P + OH^-$	$P = \frac{k_1 k_3 [S][B]}{[HS](\sum k_i[B])}$	Expression applies when $k_3 \gg k_2[BH^+]$ ; rate-controlling step is formation of S <sup>-</sup> ; P written for presence of several Bronsted bases.
VI. General base	$HS + B \xrightleftharpoons[k_2]{k_1} S^- + BH^+$ $S^- + BH^+ \rightarrow P + B$	$P = \frac{k_1 k_3 [S][B]}{(k_2 + k_3)}$ or $P = k[S][B]$	Protolytic case yields general base catalysis regardless of relative sizes of $k_2$ and $k_3$ .

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Adapted from Laidler, K. J., *Chemical Kinetics*, McGraw-Hill, New York, 1965.

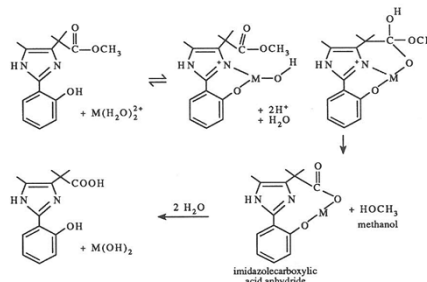


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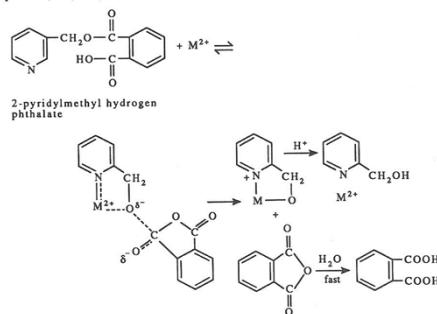
### Mechanisms 3

Pg.175

#### h Metal ion assisted hydrolysis of a methyl imidazole



#### i Ester hydrolysis by metal ion stabilization of transition state



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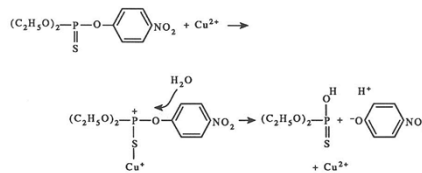
Figure 4-1 (continued).

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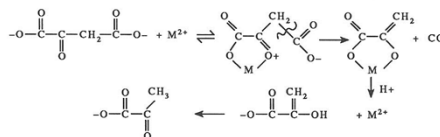
### Mechanisms 4

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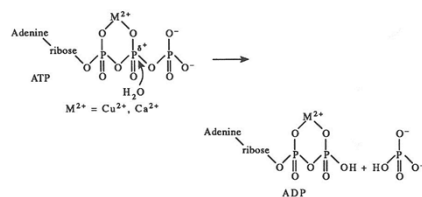
#### j Cu(II) assisted hydrolysis of parathion



#### k Decarboxylation of oxaloacetate



#### l Metal ion-catalyzed hydrolysis of ATP



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Figure 4-1 (continued).

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□ To next lecture